DEVELOPMENT OF INTEGRALLY SKINNED POLYSULFONE ULTRAFILTRATION MEMBRANE: EFFECT OF CASTING PARAMETERS

by

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LIST OF SYMBOLS

		Unit
A	Membrane area	(m^2)
C_f	Concentrations of solute in the feed	(ppm)
C_p	Concentrations of solute in the permeate	(ppm)
J	Pure water flux/PEG flux	(L/m^2h)
J_s	Solute flux	(L/m^2h)
J_w	Pure water flux	(L/m^2h)
N	Normality	(-)
P	Pressure	(N/m^2)
Q	Quantity of permeate collected	(L)
R	PEG rejection	(%)
R_m	Membrane resistance	(m^{-1})
R_c	Cake resistance	(m^{-1})
X_1	Membrane nominal thickness	(μm)
X_2	Casting speed	(rpm)
X_3	Evaporation time	(s)
X_4	Pressure	(bar)
X_5	Molecular weight of PEG	(Da)
Y_1	PEG flux	(L/m^2h)
Y_2	PEG rejection	(%)

Greek letters

ΔC	Concentration gradient	(ppm)
ΔE	Electrical potential gradient	(V)
ΔP	Pressure drop	(kPa)
t	Sampling time	(hr)
ΔT	Temperature gradient	(K)
v	Constant of non-Newtonian behavior	(-)
w	Constant of fluid consistency	(-)
γ	Shear rate	(s^{-1})
τ	Shear stress	(kg/ms^2)
μ	Viscosity	(kg/ms)

LIST OF ABBREVIATION

AFM	Atomic Force Microscopy
ASTM	American Standard Tests Method
Au	Aurum
$BaCl_2$	Barium Chloride
D	Dialysis
DD	Diffusion Dialysis
DMAc	N-N-dimethylacetamide
DMF	N,N-dimethylformamide
DMSO	Dimethylsulfoxide
ED	Electrodialysis
GS	Gas Separation
I_2	Iodine
KI	Potassium Iodide
MC	Membrane Contactors
MD	Membrane Distillation
ME	Membrane Electrolysis
MF	Microfiltration
MP	Morpholine
MW	Molecular Weight
MWCO	Molecular Weight Cut Off
NF	Nanofiltration
PALS	Positron Annihilation Lifetime Spectroscopy
NMP	1-methyl-2-pyrrolidone

PEG	Polyethylene Glycol
PES	Polyethersulfone
Pd	Palladium
PSD	Pore Size Distribution
PSF	Polysulfone
Pt	Platinum
PV	Pervaporation
PVC	Polyvinylchloride
PVP	Polyvinylpyrrolidone
PWP	Pure Water Permeability
Rh	Rhodium
RO	Reverse Osmosis
R&D	Research and Development
SEM	Scanning Electron Microscopy
TIPS	Thermally Induced Phase Separation
UF	Ultrafiltration
VP	Vapour Permeation

PEMBANGUNAN MEMBRAN PENURASAN ULTRA POLISULFONA BERSELAPUT INTEGRASI: KESAN PARAMETER PENEBARAN

ABSTRAK

Tesis ini memfokuskan pada pembangunan membran penurasan ultra polisulfona berselaput integrasi dan juga kesan parameter penebaran terhadap prestasi membran untuk menghasilkan membran yang konsisten dan reproduksi. Pembuatan membran berlapisan rata telah dilakukan dengan mengubahsuai kepekatan polimer, ketebalan nominal membran, masa penyejatan dan kadar ricih, di mana ianya telah dikenalpasti sebagai parameter penebaran yang paling mustahak untuk mengawal ketebalan dan penyatuan selaput. Dengan mempertimbangkan fakta-fakta tersebut dimana ciri-ciri dan reproduksi membran adalah sensitif kepada keadaan pembuatan, parameter untuk menghasilkan membran harus dikawal dengan lebih tepat dan ini tidak boleh dicapai dengan kaedah lama atau proses penebaran secara manual.

Oleh yang demikian, untuk mengurangkan ralat penebaran secara manual, membran telah dibuat secara konsisten dengan menggunakan Mesin Penebaran Membran Automatik yang menggabungkan ciri kemajuan dalam teknologi penebaran untuk penghasilan membran yang rata, licin, berkulit ultranipis, bebas kecacatan dan tinggi kadar reproduksinya. Mesin penebaran mempunyai empat bahagian utama dan semua parameter ini boleh disesuaikan mengikut keperluan produk akhir. Larutan penebaran dalam penyelidikan ini mengandungi polisulfona (PSF) sebagai polimer dan 1-metil-2-pirrolidona (NMP) sebagai pelarut. Polivinilpirrolidona (PVP) digunakan sebagai bahan tambahan pada peringkat awal. Di peringkat ini, kesan kepekatan PSF telah diselidik untuk mencari formula yang dapat memberikan prestasi terbaik terhadap membran. Didapati bahawa penggunaan PVP yang mempunyai berat molekul yang tinggi memberikan hasil telapan yang baik tetapi penolakan yang sebaliknya. Oleh itu

polietilena glikol (PEG) yang mempunyai berat molekul yang lebih rendah dipilih untuk menggantikan PVP sebagai bahan tambahan baru untuk meningkatkan penolakan membran. Formula PSF/NMP/PEG dengan ini digunakan dalam keseluruhan penyelidikan.

Kajian yang sistematik telah dijalankan untuk menyiasat kesan parameter penebaran termasuk ketebalan membran, masa penyejatan dan kadar ricih. Membran yang optimum boleh dihasilkan dengan kadar ricih 277.78s^{-1} dan ketebalan nominal membran 150 μm dengan masa penyejatan di antara 10s hingga 15s. Didapati bahawa hasil telapan air tulen (PWP), hasil telapan dan penolakan PEG adalah masing-masing 40.52 L/m^2h, 36.97 L/m^2h dan 73.14%. Membran yang terhasil ini kemudiannya dicirikan dengan potongan berat molekul (MWCO), pengagihan saiz liang (PSD) dan mikroskop elektron imbasan (SEM). Untuk menerangkan potensi penurasan ultra dan untuk menjangkakan perlakuan membran tersebut, hasil telapan dan penolakan menembusi membran telah diramalkan berdasarkan persamaan model linear. Kedua-dua data hasil telapan dan penolakan adalah sangat bersesuaian dengan model, dimana perbezaan di antara data eksperimen dan data yang dikira adalah sangat kecil. Kesimpulannya, prestasi akhir membran adalah sangat bergantung kepada parameter penebaran.

DEVELOPMENT OF INTEGRALLY SKINNED POLYSULFONE ULTRAFILTRATION MEMBRANE: EFFECT OF CASTING PARAMETERS

ABSTRACT

This thesis focuses on the development of integrally skinned polysulfone ultrafiltration membranes and the effect of casting parameters on the membrane performance to produce a consistent and reproducible membrane. Formation of the flat sheet membrane had been performed by alteration of polymer concentration, membrane nominal thickness, evaporation time and shear rate, which were identified as dominant casting parameters in controlling skin thickness and skin integrity. In view of the fact that membrane properties and reproducibility are sensitive to the fabrication conditions, the parameters to produce a membrane should be controlled in a more precise manner which could never be achieved using conventional or manual casting process.

Thus, to reduce the error of manual casting, the membrane was consistently fabricated using the lab developed Membrane Auto Casting Machine which combines the advantageous features of casting technology which enhances the production of even, smooth, ultrathin, defect-free membrane and high reproducibility. This casting machine basically consists of four major parts and all these parameters could be adjusted according to the requirements of final product. Casting solution developed in this study consisted of polysulfone (PSF) as a polymer and 1-methyl-2-pyrrolidone (NMP) as a solvent. Polyvinylpyyrolidone (PVP) was used as an additive at the preliminary stage. Effect of PSF concentration was studied as the preliminary work to find out the best formulation that gives the best performance to the membrane developed. It was found that the used of PVP with higher molecular weight, will give a good permeability but poor rejection. Thus, polyethylene glycol (PEG) with lower molecular weight was chosen to replace PVP as a new additive to increase the

membrane rejection. Therefore, the formula of PSF/NMP/PEG was used in the overall research.

In this study, a systematic work was carried out to investigate the effect of casting parameters including membrane thickness, evaporation time and shear rate. The optimum membrane could be fabricated under shear rate of 277.78s^{-1} for membrane nominal thickness of 150 μm and evaporation time in the range of 10s to 15s. It was determined that the pure water permeability (PWP), PEG flux and PEG rejection were 40.52 L/m^2h, 36.97 L/m^2h and 73.14% respectively at those conditions. The membranes were then characterized by molecular weight cut off (MWCO), pore size distribution (PSD) and scanning electron microscopy (SEM). Finally, in order to fully realize the potential of ultrafiltration membrane and to predict the membrane performance, the flux and rejection through the membrane was predicted based on linear model equation. Both flux and rejection data were well predicted by the model, which showed only a small difference between the experimental data and calculated data. As a conclusion, the final performances of the membrane are very much depending on the casting parameters.

CHAPTER ONE
INTRODUCTION

1.1 Research overview

1.1.1 Membrane technology

Over the past three decades, membrane processes have been adopted to perform variety of separation operations by different industries. The efficiency as well as the economics of the various industrial processes can be greatly improved if the membrane processes are suitably integrated in the exiting process, particularly, where fractionation of a set of components is more desired than total conversion or separation (Chaturvedi *et al*., 2001).

Membrane technology began in 1960. Aided substantially by several key technical breakthroughs, membrane processes have come to compete favorably with more established technologies in such areas such as water desalting, water purification and gas separation. Several new membrane based industries have been established, and membrane research and development (R&D) is now being intensely pursued in the principal industrial countries (Torrey, 1984).

The process industries produce a wide variety of chemicals and components which presents the manufacturer with a need for separation, concentration and purification of a range of materials. The last 30 years have seen the introduction of a range of separations based on one simple concept, a membrane to supplement or replace techniques of distillation, adsorption, extraction, crystallization etc (Scott, 1996).

The use of membranes for separation is one of the most important recent developments in process engineering and environmental protection. These advanced filtration processes utilize the separation properties of a polymeric or inorganic film for the membrane. The permeability of solutes at such films depends primarily on size, charge and dielectric effects (Bowen and Doneva, 2000).

1.1.2 Membrane potential and its current status

In the last decades, it has been shown that separation using membranes is a promising process when compared to the traditional ones. However, in order to increase its potential, it is necessary to obtain more efficient membranes, i.e. more selective membranes with higher permeability coefficients. On the other hand, one must consider that the use of high selectivity polymers, often leads to low permeability coefficients. Thus, in order to compensate a low permeate flux, membranes with asymmetric morphology and thin dense skin are more suitable. These membranes are normally prepared by phase inversion using the immersion precipitation technique (Pereira *et al*., 2001).

Membrane has been applied commercially to separate individual components from mixtures of liquids and gases. The membranes are non-porous thin layers on porous substrates. All these properties are relative in terms of individual process and the respective capital and operating costs. Chemical resistance relates more to the operating lifetime of the membrane. A gradual deterioration of the membrane can occur over months and years with perhaps only a relatively small loss of selectivity. The initial membrane costs and cost of refitting can determine the material chosen (Scott, 1996). The functioning of the membrane will depend on its structure as this essentially determines the mechanism of separation and thus the application. Two types of structures are generally found in membranes (solid material); symmetric or asymmetric.

The membrane processes have been greatly developed in the last decades within different industries. The development of new applications using synthetic membrane requires polymers with outstanding properties. The polymer materials not only have to resist acids, bases, oxidants or reductants, high pressures and high temperatures, but also have appropriate chemical properties so as to lead to high flux and high selectivity membranes for the foreseen applications (Park *et al*., 1999).

Membrane separation processes has become one of the emerging technologies, which have undergone a rapid growth during the past few decades. A membrane is defined as a selective barrier between two fluid phases (Sirkar and Ho, 1992; Pandey and Chauhan, 2000). There are six major membrane processes, which are widely used, in industrial application. They are microfiltration, ultrafiltration, reverse osmosis, electrodialysis, gas separation and pervaporation. The key membrane performance variables are selectivity, permeability and durability. For solution diffusion membranes, permeability is defined as the product of the solubility and diffusivity. The most important membrane qualities are high selectivity, high permeability, mechanical stability, temperature stability and chemical resistance.

In membrane technology, the most important goals are to control membrane structure and thus membrane performance (flux and rejection). This objective is not easy to achieve because of membrane structure and performance depend upon different factors like polymer choice, composition and temperature of coagulant dope solution among others. Thus, in this study, a systematic study was currently carried out to investigate effects of polymer concentration, membrane thickness, forced-convective evaporation time and shear rate in developing asymmetric membranes with superior separation performance. Furthermore, by changing one or more of these variables, which are dependent on each other, membrane structure can be affected quite significantly.

1.1.2 Advantages of membrane technology

Membrane separation processes are highly innovative process engineering operations. Certain types of materials are inherently difficult and expensive to be separated. Hence, membrane technology would be promising in the future and can offer an alternative to the conventional industrial separation methods. Recently, membrane separation processes are increasingly important and popular in industries and have become attractive alternatives to conventional methods such as absorption, distillation, extraction, leaching, crystallization and adsorption etc. They offer a number of significant advantages and attractions over competing technologies.

Membrane nowadays have gained wide acceptance and made significant inroads against competing technologies in many areas because of flexibility and performance reliability of membrane system, cost competitiveness, increasing demand and environmental awareness. Besides that, the advantages using polymer membranes are good processability, inexpensive production and low operating cost (relatively low capital and running costs) and modular design (construction). In short, they offer low capital cost, low energy consumption, ease of operation and cost effectiveness.

Microfiltration and ultrafiltration are suitable for clarification and disinfection because they act as absolute physical barriers. There is a tendency to prefer UF to MF because of its higher separation efficiency and less sensitive to pore clogging. This also makes UF more interesting as a pretreatment step for reverse osmosis (Doyen, 1997). Microfiltration, in combination with ultrafiltration can also solve almost any separation problem involving particulate material and macromolecules. Major technical advantages of these filtrations are that they are well suited to temperature sensitive materials and are not chemically altered as in competitive procedures such as precipitation and distillation. Membrane filtration also offer relative simplicity of

operation and low costs in comparison to centrifugal separation, vacuum filtration and spray drying (Scott, 1996).

The other technical advantages of membrane separations, which result in economic advantages, are that they frequently achieve higher efficiency of separation, they often yield faster separations and the simplicity of operation in modern compact modules means operation with small or large plant is relatively easy (Scott, 1996). Membrane systems are economic viability and flexibility since they can be easily scaled down for operation at partial capacity or scale up by adding membrane modules in stages to accommodate higher capacities (Lai, 2002). Membrane separation technology is also promising safety effect with a relatively low environmental impact because they contain no toxic material (Lonsdale, 1982; Lai, 2002).

1.2 Problem statement

One of the major problems confronting the use of membrane based separation processes in a wide range of applications is the lack of membranes with high flux and high selectivity. During fabrication, membrane formation process plays an important role and certain factors need proper attention in order to produce a good separation membrane.

Currently, membrane separation technologies are challenged to maintain their favorable economics while improving their selectivity, flux and durability. (Kawakami *et al*., 1996). It had been proved that there has been a trade off between selectivity and permeability; high selectivity tends to exhibits less permeability and vice versa. It has been a common problem to produce a membrane that is high in rejection but low in water permeability or vice versa. A high rejection membrane is normally denser because of thicker skin layer, which result in the poorer water permeability. On the other hand, the thinner skin and porous skin layer most probably provide higher flux but

poorer rejection due to structural stability problem. Therefore the membrane performance should be optimized in such a way to enhance other advantages features of membrane.

The conventional membrane has been traditionally used without knowing the relationship between the structural properties of the membrane and its performance. The membrane is normally reported in terms of their phenomenological properties such as solute permeability constant, pure water permeability and molecular weight cut off. This information is not based on the mechanistic structure of membrane, as a result the membrane performance is structurally impractical to be optimized.

Therefore, to produce a good membrane quality and performance, the techniques and parameters to control the membrane properties are crucial to be studied and identified. The knowledge in the material selection, solution preparation, preparation environment and technique that contributes to the final morphology of the membrane should be fully understood. However, this information cannot be fully accessed in the literature. Therefore, it is very important to study the basic of membrane formation process and relate to its performance through the engineering perspective. A consistent and reproducible membrane layer is needed. They should allow maximum flux but could resist the compressibility due to pressure and the pore size should be narrow distributed. Casting parameters such as polymer concentration, shear rate, membrane nominal thickness and evaporation time are hence playing an important role to determine its final performance. Membrane formulation itself can also affecting the performance, thus precise work should be carried out in order to develop a good membrane.

It is a problem to obtain the above characteristic if the polysulfone membrane is prepared manually because hand-casting could not provide consistent shear rate and

thickness. Therefore, Membrane Auto Casting Machine that exhibits more advantageous features compared to the manual casting method was used. Casting speed of the system can be adjusted accordingly into shear rate needed to suit the polymer solutions with different viscosities. This could control the morphology of the membrane produced. Besides that, prominent surface even-ness could be achieved by using doctor blade that is flat compare to the stainless steel casting blade. The other advantage of doctor blade is its low cost and disposable compared to normal casting blade. All the casting process guided along by a ball screw. Furthermore this Membrane Auto Casting Machine has an ability to produce a larger piece of membrane with adjustable thickness as required compared to the manual casting. Thickness control therefore would save the thickness setting time. The properties of the skin layer depend on the forced-convective flow air across the membrane surface and these properties could be manipulated by the evaporation speed and time. Therefore, it is important to use a casting machine that could perform the casting in a more consistent manner. The parameters studied could be optimized if only the process run automatically.

Membrane skin layer and morphology is very sensitive. The rejection, selectivity and permeation ability depends on the skin layer and its structure. Membrane permeability is directly proportional to the skin thickness. Different distribution of skin thickness would cause a local different in the flux. The shear rate of casting process will affect the viscosities of polymer which eventually determine the structure stability. Surface even-ness and smooth casting process will determine the porosity of the membrane, while evaporation rate and time are crucial for obtaining a dense and thin skin layer. The parameters to produce an optimum membrane therefore should be controlled in a more precise mode. Quantitative analysis on the reproducibility of the membrane could contribute to advancement of membrane science and technology in the future as well as application in industry.

1.3 Objectives of research

The objectives of this study are stated as following:

1) To develop and produce an integrally skinned asymmetric ultrafiltration membrane using Membrane Auto Casting Machine to reduce the error of manual casting and enable the casting to be carried out under optimum condition.
2) To study the polymer concentration in order to find out the best formulation that gives the best performance of the membrane developed in the preliminary study.
3) To study the effect of casting parameters such as membrane nominal thickness, shear rate and evaporation time and also the effect of operating pressure on membrane characteristics and performance.
4) To characterize the membrane developed on liquid permeation measurement (Pure water flux/ solute flux, solute rejection, molecular weight cut off (MWCO), scanning electron microscopy (SEM) and pore size distribution (PSD).
5) To make a comparison between experiment data with linear model calculation data in order to confirm and to verify both of data to fit each other efficiently.

1.4 Scopes of study

The technique to produce the ultrafiltration membrane was clearly discussed in this study. The polysulfone ultrafiltration membrane is prepared using polysulfone/1-methyl-2-pyrrolidone/polyethylene glycol (PSF/NMP/PEG) system. The polymer solution is casted at different nominal thickness, shear rate and evaporation time. To make sure the casting process is operating under consistent and efficient condition, a Membrane Auto Casting Machine was used so that it could precisely control the nominal thickness, shear rate of casting and forced-convective evaporation system. Compared to the manual casting method, the Membrane Auto Casting system has

more advantageous features than the conventional casting. The porous structure of polysulfone layer is formed by phase inversion-immersion precipitation method.

Several casting parameters to produce the ultrafiltration membrane are outlined here such as membrane thickness, shear rate and evaporation time. The membrane performance in terms of flux and rejection were then evaluated for every effect. This was done by filtration measurements with PEG solutes having different molecular weights of 3000, 6000, 10,000, 20,000 and 35,000 Dalton to test its performance. The membrane performance is further tested at different pressure; 1, 1.5, 2, 2.5 and 3 bar.

The influence of the membrane nominal thickness of 100μm, 150μm and 200μm on flux and rejection characteristics was studied. Different shear rate varies from 83.88s^{-1} to 486.67s^{-1} at the three membrane nominal thickness was also studied. For such a constricted evaporation time; 0, 5, 10, 15 and 20s, the effect of evaporation time on membrane properties and performance should be more understood.

The membranes prepared under these parameters are characterized in terms of membrane structural properties such as pore size distribution and characterization of the membrane surface morphology and structure using SEM to compare the membrane at different parameters studied. The MWCO value is also determined in this study.

1.5 Organization of the thesis

There are five chapters in this thesis and each chapter gives the important information of this research. An introduction of membrane technology, membrane potential and its current status and the advantages of membrane technology are outlined in Chapter 1.

Chapter two presents a review of the literature. It is divided into six major sections. The first section gives a review about the membrane definition and then followed by descriptions of membrane classification which is divided into asymmetrical and symmetrical membrane in section two. A brief explanation about the types of membrane processes were given in section three. Section four focused on the types of membrane process used in this study which is ultrafiltration membrane. The historical background and the development of the UF membrane were reviewed followed by the basic principles and the application of UF. Section five described about membrane formation process. There are various methods for making very thin membranes and method selected in this study are the phase inversion or Loeb Sourirajan method by immersion precipitation technique. Section six explains detailed on the development of the integrally skinned ultrafiltration membrane. In this section the material selection and the development of the porous support layer were well discussed. Effect of casting parameters that divided into four major effects on polymer concentration, membrane nominal thickness, shear rate and evaporation time were well explained in section seven while the final section was the study on membrane properties.

Chapter three covers the experimental part of the research whereby the laboratory scale of membrane synthesis, characterization and performance were discussed. The synthesis method for developing polysulfone ultrafiltration membrane using Membrane Auto Casting Machine is discussed in detail. The characterization methods for membrane properties like liquid permeation measurement (flux, rejection,

MWCO determination) and SEM analysis also pore size distribution were outlined. The procedures to carry out the permeation test in dead-end filtration unit were explained in detail.

Chapter four presents all the acquired results and gives an explanation for the finding and discussion. It is grouped into four main sections; section one presents the preliminary study on the effect of polymer concentration on the membrane performance while section two presents the results of development of integrally skinned polysulfone ultrafiltration membrane: effect of casting parameters (membrane nominal thickness, shear rate and evaporation time) followed by the effect of process parameters (pressure and MWCO) on membrane performance in section three. Finally section four shows the comparison between experiment data with model linear calculation data. In short, the experimental studies are carried out based on the objectives outlined in Section 1.3.

Finally Chapter five gives the conclusion and some recommendation for future research. The conclusion is written according to the finding found in Chapter four. Based on the conclusion, recommendation for future work was suggested.

CHAPTER TWO
LITERATURE REVIEW

2.1 Membrane definition

During the last three decades, membrane filtration has emerged as a separation technology which is competitive in many ways with conventional separation techniques, such as distillation, adsorption, absorption, extraction etc. A membrane can be described as a thin barrier between two bulk phases that permits transport of some components but retain others. A driving force is necessary to allow mass transport across the membrane. The two phases separated by the membrane, i.e., the feed and the permeate, can be present in the liquid or in the gaseous state. The driving force that is necessary for the transport is a transmembrane pressure gradient ΔP, a concentration gradient ΔC, an electrical potential gradient ΔE, or a temperature gradient ΔT (Beerlage, 1994). A schematic drawing illustrating a membrane separation process is given in Figure 2.1.

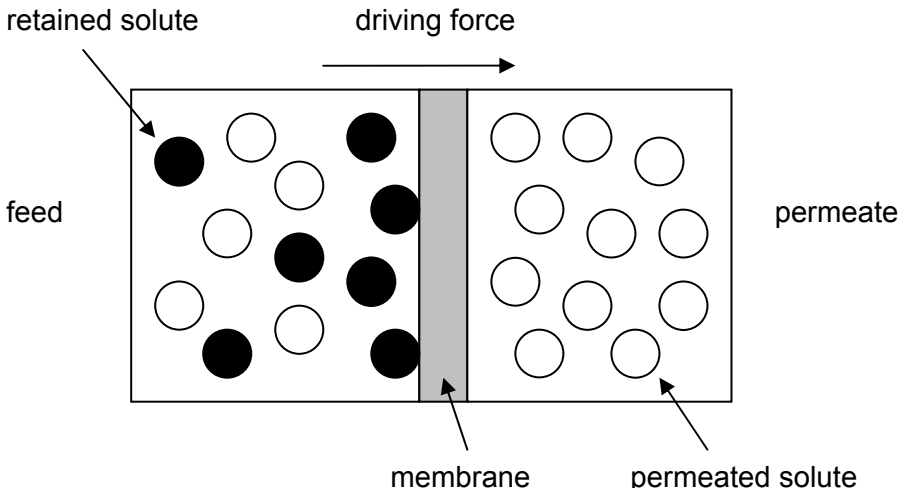

Figure 2.1 Schematic drawing illustrating a membrane separation process (Beerlage, 1994)

A membrane is also defined as a thin sheet of natural or synthetic material which is permeable to substances in solution (Torrey, 1984). A permeable or semi-permeable phase of membrane is often a thin polymeric solid, which restricts the motion of certain species (Scott, 1996). Indeed, as we have seen, approximately 60% of synthetic polymeric membranes are today employed as semipermeable barrier layers which permit certain components of solutions or suspensions to permeate more rapidly than others (Kesting, 1985). This added phase is essentially a barrier between the feed stream for separation and one product stream. This membrane or barrier controls the relative rates of transport of various species through itself and thus, as with all separations, gives one product depleted in certain components and second product concentrated in these components (Scott, 1996).

The performance of a membrane is defined in terms of two simple factors, flux and selectivity for solutes and particles in liquids and gases. Flux or permeation rate is the volumetric (mass or molar) flow rate of fluid passing through the membrane per unit area of membrane per unit time or in another words, the absolute rate at which a permeate traverse. Selectivity or retention is defined as the fraction of solute in the feed retained by the membrane (Scott, 1996).

2.2 Membrane classifications

There are many ways to classify a membrane. Basically membranes can be classified as symmetric or asymmetric. Figure 2.2 summarized the membrane classifications.

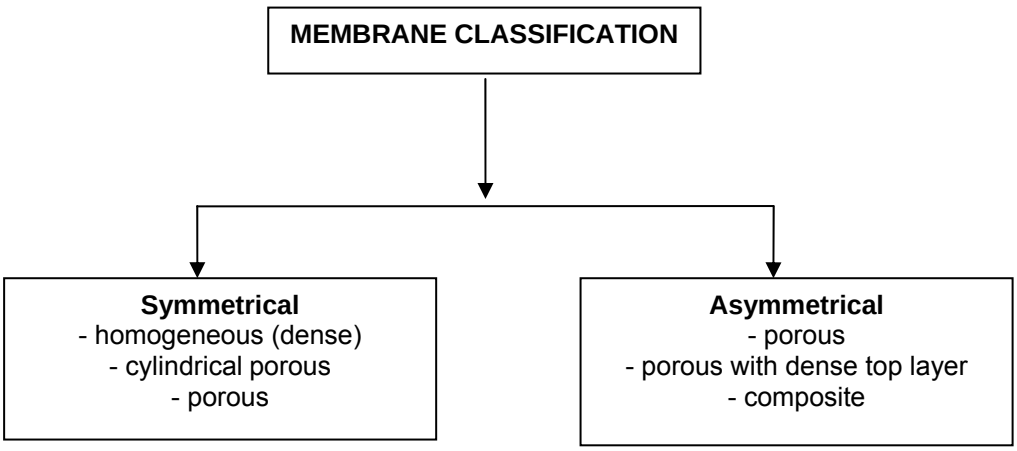

Figure 2.2 Membrane classifications (Ismail *et al.,* 2002b)

2.2.1 Asymmetrical membrane

The asymmetrical membrane classification is divided into two:

1) Phase inversion membrane in which the porous structure is produced by precipitation from a homogeneous polymer. The membrane is made up of a thin, dense skin (active layer) with a porous support layer underneath.

2) Composite membrane which has an active (skin) layers form on the porous support. Both the layer might be from different materials which are selected for optimum function (Baker, 2000).

An asymmetric membrane generally consists of a thin, selective skin layer, supported by a porous substructure. For an asymmetric membrane, its skin layer must be almost defect-free to assure that permeation is exclusively controlled by a solution/diffusion mechanism to achieve the maximum permselectivity, and its skin layer must be as thin as possible to maximize the membrane productivity. Since the dense skin layer is formed by a phase inversion process which occurs by bringing an initially thermodynamically stable polymer to an unstable state during the coagulation step, the complicated mass transfer and solvent exchange during the demixing generally yield defective skin layers (Chung *et al.,* 2000).

2.2.2 Symmetrical membrane

Symmetrical membranes can be microporous or nonporous. A microporous membrane is very similar in structure and function to a conventional filter. It had a rigid, highly voided structure with randomly distributed, interconnected pores. However, these pores differ from those in a conventional filter (Baker, 2000).

Thus it is clearly shows that the difference between these two types is the presence of a pore size gradient in asymmetric membranes: the pores in the toplayer have a different size compared with the pores at the bottom side. It is also possible that the toplayer is non-porous, or even made of a different material in so-called composite membranes. In porous symmetric membranes, the pores can either form long channels, or the membrane can have a porous sponge-type structure; a symmetric membrane can also be non-porous, i.e., a homogeneous film. Most ultrafiltration membranes have an asymmetric structure; they are porous with a porous toplayer. Both polymers and inorganic materials are used for the preparation of membranes (Beerlage, 1994).

2.3 Membrane processes

Membrane processes are used in a wide range of applications and the number of such applications is still continuing to rise. Many types of membranes have been developed and commercialized. Membranes can be classified with hollow fiber and flat sheet membranes, these processes are classified based on various factors such as nature of driving force, membrane itself (its structure, as well as the material), type of feed and its application (gas or liquid separation). Membrane processes such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), dialysis (D), electrodialysis (ED), membrane electrolysis (ME) and diffusion dialysis (DD) are considered as first generation processes; whereas, second generation

processes are gas separation (GS), vapour permeation (VP), pervaporation (PV), membrane distillation (MD), membrane contactors (MC) and carrier mediated processes (Beerlage, 1994). The selected membrane processes is summarized and shown in Table 2.1.

Table 2.1 Membrane processes (Beerlage, 1994)

Process	Pore size, nm	Materials retained	Materials passed	Pressure, bar
MF	> 50	Particles (bacteria, yeasts etc)	Water, salts, macromolecules	< 2
UF	1-100	Macromolecules, colloids, latices solutes MW>10,000	Water, salts, sugars	1-10
NF	~ 1	Solutes MW>500, di- and multivalent ions	Water, sugars, monovalent ions	5-20
RO	Not relevant	All dissolved and suspended solutes (sugars, salts)	water	15-80

Modern membrane separation processes moved ahead rapidly with the discovery of methods for making effectively very thin membranes. This was crucial to the rapid commercialization of reverse osmosis (RO), ultrafiltration (UF), and gas separations, and it was important in microfiltration (MF) as well.

Membrane process can be operated in two major modes according to the direction of feed stream relative to the orientation of the membrane surface: dead-end filtration and crossflow filtration. The majority of the membrane separation applications use the concept of crossflow where the feed flows parallel to and past the membrane surface while the permeate penetrates through the membrane overall in a direct in normal to the membrane. Predominant in the conventional filtration processes, dead-end filtration is used in membrane separation only in a few cases such as laboratory

batch separation. In this mode, the flows of the feed stream and the permeate are both perpendicular to the membrane surface (Hsieh, 1996).

2.4 Ultrafiltration (UF)

The term ultrafiltration (UF) has changed its meaning over the years. UF referred to filtrative separation of particles in the colloid-size range. In UF the dispersed phase ("solute" in its most general sense) passes through the membrane less readily than the "solvent" for one of several reasons (Kesting, 1985; Ghose *et al.,* 2000; Ochoa *et al.,* 2001):

1. It is adsorbed in the surface of the filter and its pores (primary adsorption)
2. It is either retained within the pores or excluded therefrom (blocking)
3. It is mechanically retained on top of the filter (sieving)

UF which lies between microfiltration and nanofiltration, is a process with the ability to separate extremely small suspended particles and dissolves macromolecules from fluids using membranes of surface pore size in the range of 1 to 100 nm. An ultrafiltration membrane acts as a selective barrier. It retains species with molecular weights higher than a few thousands Dalton (macrosolutes), while freely passing small molecules (microsolutes and solvent). The separation is achieved by concentrating the large molecules present in the feed on one side of the membrane, while the solvent and microsolutes are depleted as they pass through the membrane. UF membranes are typically rated by molecular weight cut off (Baker *et al.,* 1991; Chaturvedi *et al.*, 2001; Hesketh, 2003).

UF is similar to reverse osmosis but it is used for retaining larger solutes with lower operating pressure. The typical operating pressure is in the range of 1-10 bars. The membrane used can be considered porous, but generally classified as asymmetric with a thin resisting top layer and a porous sub-layer. UF membrane are often operated

in a tangential flow mode where the feed stream sweeps tangentially across the upstream surface of membranes as filtration occurs, thereby maximizing flux rates and membrane life. UF generally has a molecular weight cut off (MWCO) of 1,000 to 1,000,000. Some properties are surface pore size, pore size distribution, % porosity, rejection, flux, temperature stability, solvent resistance and pressure resistance. Retentivity is important and the skin plays an important role. It should provide a high flux rate and prevent the internal pore blockage that can severely affect the performance (Hesketh, 2003).

UF is a pressure-driven membrane transport process that has been applied, on both the laboratory and industrial scale. The use of UF membranes for the separation of dissolved molecules of different size and nature has seen an increased interest in recent years. Depending on their pore size, UF technology has received tremendous importance for separation, concentration, purification and fractionation of various products in a diverse fields, such as removal of particulates from air, filtration of colloidal suspensions, treatment of product streams in the food and beverage industry, recovery of useful material from coating or dyeing baths in the automobile and textile industries and treatment of industrial waste waters, also in medical, biotechnological industries, paper industry, dairy industry, etc. (Baker *et al*., 1991; Khan *et al.*, 2000; Reddy *et al.,* 2003).

UF membranes also serve as supports for ultrathin reverse osmosis and nanofiltration (composite) membranes. Asymmetric UF membranes consist of a thin, dense top layer (the skin), which is responsible for the selective rejection of solutes molecules, and a more open, porous substructure that does not affect the membrane performance negatively. The most important characteristics of these membranes are the thickness of top layer (hydrodynamic resistance) and the pore structure (mean pore size and pore size distribution) of the skin. In order to develop and subsequently use

the most appropriate membrane for a certain application, one has to determine the features just mentioned above, using independent characterization methods. Amongst these are pure water flux or gas permeability, scanning electron microscopy (SEM) and molecular weight cut off (MWCO) measurements (Smolders *et al*., 1992).

Asymmetric UF membranes have been casted from a number of polymers including cellulose acetate, polycarbonate, polyvinylchloride, polyamides, modacrylic copolymers (e.g., PVC, acrylonitrile, and styrene-acrylic acid copolymers), polysulfones, halogenated polymers (such as polyvinylidene fluoride), polychloroethers, acetal polymers, acrylic resins, and various polyelectrolytes. Membranes with remarkable solvent resistance, pH resistance, chemical resistance, thermal and mechanical stability; also high flux and selectivity, high durability (longest possible life) and of course material cost are on the market today (Schweitzer, 1997).

Many researchers try to modify the skin layer of asymmetric membrane to get an ultrathin and defect-free layer which is the requirement for high rejection and high flux. It is important that the polymeric solution must have high enough viscosity to overcome the osmotic pressure occurring at the contact of the polymeric solution with a nonsolvent so that the surface of the membrane may be free from defect. Careful control should be performed so that an optimum membrane which is ultrathin (high flux), defect-free (high rejection) and macrovoid free (high mechanical strength) can be obtained.

2.4.1 Historical background and development of ultrafiltration membrane

Nowadays, membrane processes are becoming increasingly attractive as an alternative to conventional water and wastewater treatment. A major obstacle in applying membrane processes for portable water supplies and wastewater treatment is the permeate flux decline due to membrane fouling. This is a problem because the

capital and operational costs of membrane systems are directly dependent on the membrane permeate flux (Bian *et al*., 2000). There have several recent developments in microfiltration and ultrafiltration system designs targeted at improving and stabilizing flux rates. These include hydrodynamic techniques to reduce polarization, such as pulsation, vortex flows and rotation and other techniques such as vibratory shear enhancement, electric fields and ultrasonics (Scott, 1996). The chronological development of ultrafiltration membrane is shown in Table 2.2.

2.4.2 Basic principles

At the moment, polymeric ultrafiltration membranes are most widely used in all kind of configurations (plate and frame, spiral, hollow fiber and tubular). These membranes are based on engineering polymers such as polysulfones, polyacrylonitriles and polyvinylidenefluoride (Doyen *et al.,* 1997).

Performance of membrane strongly depends on the permeability and selectivity of the membrane. Membrane with higher permeability leads to higher productivity and lower capital costs whereas membrane with higher selectivity leads to higher recovery and lower power cost. Indeed, membranes that simultaneously posses high values of selectivity and permeability would lead to the most economical separation process. Unfortunately, there is usually a trade off between permeability (skin thickness) and selectivity (skin integrity), where both parameters tend to exhibit an inverse or contradictory relation, representing a major problem in production and application of commercial separation membranes (Datta *et al.*, 1992; Clausi and Koros, 2000).

Table 2.2 Chronological development of ultrafiltration membrane

Year	Development/performance	Reference
1748	- Abbé Nolet coined the word osmosis to describe permeation of water through a diaphragm	Baker *et al.* (1991)
Prior to 1960	- interest in membranology was primarily concentrated in academic circles and membranes were used as laboratory tools to develop physical/chemical theories	Kesting (1993)
1846-1869	- cellulose nitrate the first synthetic (or semisynthetic) polymer was studied and produced commercially by Schoenbein	Kesting (1993)
1869	- Lhermite contributed the concept of solution, that is, membrane-permeant interaction, to membrane permeation theory	Kesting (1993)
1872	- the first flat membranes were prepared by Baranetzky	Kesting (1993)
1887	- measurements of solution osmotic pressure with membranes by Traube and Pfeffer were used by van't Hoff to develop limit law and explaining the behavior of ideal dilute solutions. - This work led directly to the van't Hoff equation and the ideal equation of state of a perfect gas. The concept of a perfectly selective semipermeable membrane was also used by Maxwell and others at about the same time when developing the kinetic theory of gases	Baker *et al*. (1991)
	- early investigators experimented with any type of diaphragm available to them, such as bladders of pigs, cattle or fish and sausage casings made of animal gut. - in later work collodion (nitrocellulose) membranes were preffered	Baker *et al*. (1991)
1906	- Bechhold devised a technique to prepare nitrocellulose membranes of graded pore size, which determined by a buble-test method. - observed that permeability varied inversely with the concentration of polymer in the solution	Baker *et al*. (1991)
1915-1917	- Brown produced a graded series of cellulose nitrate membranes by swelling initially dense films in alcohol-water solutions of varying concentration. - employ cellulose acetate as a membrane polymer and to note the inhomogeneity in depth which was later to prove of great importance to the development of RO, UF, and gas separation membranes	Kesting (1993)
	- early attempts to control and vary porosity were large empirical - Bigelow & Gemberling studied the effects of drying time	Kesting (1993)
1927	- the former were the basis for the first commercial microfiltration membranes which appeared in Germany	Kesting (1993)
early 1930s	- microporous collodion membranes were commercially available.	Baker *et al*. (1991)

Table 2.2 Continued

Year	Development/ performance	Reference
1950s	- MF membrane technology was expanded to other polymers, particularly cellulose acetate, and membranes found their first significant applications in the filtration of drinking water samples at the end of World War II	Baker *et al*. (1991)
1960	- the elements of modern membrane science had been developed, but membranes were used in only a few laboratories and small, specialized industrial applications - there was no significant membrane industry and total sales of membrane for all applications probably did not exceed $20 million per year - membranes suffered from 4 problems that prohibited their widespread use: 1) they were too unreliable, 2) too slow, 3) too unselective, 4) too expensive. - partial solutions to each of these problems have been developed during the last 30 years, and as a result there is a surge of interest in membrane-based separation techniques	Baker *et al*. (1991)
1960-1980	- the invention by Loeb & Sourirajan of the first asymmetric cellulose acetate RO membrane - this development was a major breakthrough in membrane technology stimulated both commercial and academic interest, first in desalination by RO, and then in other membrane applications and processes - membrane separation transformation from a laboratory to an industrial process development - Loeb-Sourirajan process for making defect-free, high flux, ultrathin RO membranes which consist of ultrathin, selective surface film supported on a microporous support that provides the mechanical strength: skin layer (0.1-1μm) overlaying on a thick and highly porous sub-layer (100-200μm with an average void size ranging from 0.01 to 1μm), where both layers are composed of the same material and formed in a single operation. The skin represents the actual selective barrier, while the sublayer serves only as a mechanical support for the skin, with negligible effects on separation - tremendous change in the status of membrane technology. Building on the original Loeb-Sourirajan membrane technology, other processes were developed for making ultrathin, high performance membranes. - using such processes, including interfacial polymerization or multilayer composite casting and coating, it is now possible to make membranes as thin as 0.1 μm or less. Methods of packaging membranes into spiral-wound, hollow fiber, capillary and plate and frame modules were also developed and advances were made in improving membrane stability.	Lonsdale (1987), Baker *et al*. (1991), Pinnau & Koros (1991), Kesting (1993), Ismail & Shilton (1998), Ismail & Lai (2002), Ismail & Yean (2002), Idris *et al*. (2002)
1980	- MF, UF, RO and electrodialysis were all established processes with large plants installed around the world	Baker *et al*. (1991)

Hence, numerous studies and efforts were centered upon development of high performance asymmetric membrane for separation. Today, new challenges are directed towards development of defect free and ultrathin skinned asymmetric membrane for gas and liquid separation process, in which further insight and dramatic progress are being made.

In recent years, a number of post-treatments, including coating or caulking technology, have been widely practiced in both academic and industry. Defects on asymmetric membrane are plugged with a highly permeable but nonselective material such as silicone rubber or polymetyhlsiloxane to increase selectivity without decreasing permeability. Nevertheless, coating process is often time consuming, inducing complexity and adding costs for continuous membrane production (Chung *et al.,* 1994). In current state of art, new challenges are directed towards development of defect-free and ultrathin skinned asymmetric membranes for separation, without imposing any additional post treatments. Hence, a comprehensive study on original concepts and new advances in membrane process are necessary to generate defect-free and ultrathin skinned asymmetric membranes with superior performance for separation.

The main factors determining the membrane behaviour in a filtration process are the structure, the chemical composition and the operation conditions. Structure, involving pore size distribution or pore density and the active layer thickness is the main factor in determining the flux and retention. However, these parameters are strongly influenced by the chemical composition of the material, which has a great influence on adsorption and fouling mechanisms in the surface and inside the pores. In the manufacture of membranes by phase inversion, it is common to add different substances, to control bath structure and chemical interactions (Marchese *et al.,* 2003)

2.4.3 Applications

Membrane technology represents one of the most effective and energy saving means amenable to a wide range of separation processes (Chan *et al*., 1997). Many ultrafiltration applications are already being practiced in industry and more are being studied.

Many applications relate to the food industry and dairy industries, pharmaceuticals and biotechnology, water purification and waste water treatment in the chemical and paper industries. For example, UF is used to recover lactalbumin and lactoglobulin from cheese whey, to pre-concentrate milk before cheese making, and for fruit juice clarification. The other important applications are the recovery of electrocoat paint and purification of water. Other applications are being studied such as recovery of precious metals such as Pt, Au, Rh, Pd, etc. These ultrafiltration applications on various industries are explained and summarized below in Table 2.3.

2.5 Membrane formation process

In general, there are several ways to prepare porous polymeric films, such as sintering, stretching, track etching and phase separation processes. The final morphology of the membranes obtained will vary greatly, depending on the properties of the materials and process conditions. The majority of membranes are prepared by controlled phase separation of polymer solutions into two phases: one with a high polymer concentration, and one with a low polymer concentration. The concentrated phase solidifies shortly after phase separation, and forms the membrane. The performance of this membrane strongly depends on the morphology formed during phase separation, and subsequent (or almost simultaneous) solidification (Van de Witte *et al.,* 1996).